

EXPERIMENTAL STUDIES CONCERNING
EQUILIBRIUM AND NON-EQUILIBRIUM SYSTEMS
IN PRE-BIOLOGICAL ATMOSPHERES

NGR
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A. Progress Report for Period 9/1/65 - 2/28/66

PART I

To fill the need for a rapid means of attaining gas-phase equilibrium for the experiments for Part I, (described above) a high energy radio-frequency plasma discharge reactor ^{2,3} has been designed and used successfully for degrading hydrocarbon gases. It should be possible with this equipment to generate a plasma consisting of radicals, ions and atoms from almost any compound having sufficient vapor pressure. Such a plasma should rapidly attain a steady state as high molecular weight products are deposited on the walls of the reactor, and when the power is turned off, the gas phase may be expected to approach an equilibrium conditions.

When methane or ethylene is subjected to the radio-frequency discharge, a deposit of polynuclear aromatic hydrocarbons, the "asphalt" phase, is formed on the walls of the reaction vessel. Only small amounts of aliphatic compounds and no more than minute traces of carbon are present. At least seven different gaseous products from methane have been indicated by gas chromatography. All of these results are consistent with theoretical predictions, and the validity of our assumption of the inaccessibility of graphite, even under the violent conditions of plasma excitation, is confirmed. As the reaction time is decreased, the ratio of the benzene-soluble (lower molecular weight) compounds to the benzene-insoluble (very high molecular weight) compounds is greatly increased.

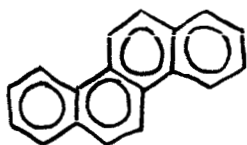
When mixtures of methane and hydrogen were treated in the reactor, it was found that the asphalt threshold existed at a H/C ratio of 7 at 20 mm. pressure. As this ratio was decreased, the rate of deposition of solids increased. As predicted by our calculations, asphalt formation occurred even in the presence of excess hydrogen

(i.e., at a ratio greater than 4) at low pressures.

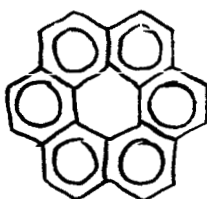
When the reactor walls were continuously cooled, complete equilibrium was apparently not attained, as the product mixtures, although highly unsaturated, contained only small amounts of aromatic compounds. The significance of these results with regard to the reaction mechanisms is being investigated. The accumulation of non-aromatic material is of particular interest in connection with the origin of petroleum from non-biological sources.

Of the various procedures investigated for isolating the aliphatic fraction from the tarry products, the most clean-cut was found to be treatment of an aliquot of material with sulfuric acid. Because of difficulties with our gas chromatograph it has been possible so far only to test the feasibility of its use for our samples. It has been found that gas chromatography, in conjunction with thin-layer chromatography and ultraviolet and infrared spectrometry, will be a valuable tool for rapid analysis of gaseous, liquid and solid samples. A Bendix time-of-flight mass spectrometer has just become available and a Varian double-focusing M-66 has been purchased by the Chemistry Department.

By means of thin-layer chromatography, paper chromatography, and ultraviolet spectrometry the polynuclear aromatic compounds, chrysene, coronene, pyrene, and fluoranthene have been identified among the constituents of the asphalt fraction.



Chrysene



Coronene



Pyrene



Fluoranthene

PART II

Since the primitive atmosphere of the earth contained little oxygen, it has been suggested that in early biological systems, and possibly in present-day anerobic bacteria, phosphite may replace some of the phosphate of oxygen-utilizing organisms. To investigate a possible clue to this aspect of primitive chemistry, a method for determining small amounts of phosphite or hypophosphite in anerobic bacteria has been worked out.

PART III

Thermodynamic calculations carried out by the group at the National Biomedical Research Foundation included a broad survey of equilibria in systems containing the elements C, H, O, N, S, P and Cl at pressures of 10^{-16} to 50 atmospheres and temperatures of 300°K to 1000°K. For some of the computations the formation of solid graphite was prohibited on kinetic grounds. The equilibria included in principle all compounds up to molecular weight 300. We have recently submitted a paper to Science, in which these data are discussed and correlated with the results of Anders' investigations of carbonaceous chondrites as well as equilibrium experiments in both our laboratories and Anders' laboratories.

Preliminary investigations were made of systems where other compounds such as N_2 , CO, CO_2 , and aromatics were also omitted from the equilibrium computations, singly and in combination.

The research accomplished over the period 9/1/65 - 2/28/66 has resulted in submission of a paper for publication. An abstract of this paper follows:

"Thermodynamic Equilibrium and the Origin of Organic Matter"

By

R.V. Eck, E.R. Lippincott, M.O. Dayhoff and Y.T. Pratt

Theoretical and experimental support is presented for the hypothesis that organic compounds occurring in carbonaceous chondrites may have formed under equilibrium or near equilibrium conditions. The equilibrium distributions of organic compounds at temperatures between 300 and 1000 K and pressures of 10^{-6} to 50 atmospheres for the C-H-O system have been computed. At high temperatures and low pressures aromatic compounds may form even in the presence of excess hydrogen. Equilibrium concentrations of numerous compounds possible at 1000° K when N, S, and Cl are added to the system have also been determined. A limited equilibrium method is employed in which those few compounds which form with most difficulty are excluded from the computations. This approach is shown to be useful in the interpretation of certain experimental data. In preliminary experiments it has been found that gases, converted to the plasma state by high energy radio frequency discharge, yield product mixtures which are in qualitative agreement with those predicted.

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